





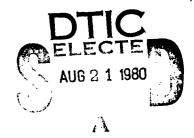
FUNDAMENTALS OF CORROSION FATIGUE BEHAVIOR OF
METALS AND ALLOYS.

Technical rept.

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ABSTRACT

It is well known that environment plays a very important role in fatigue failures. In some cases only crack propagation rates are affected; however, for many others all of the steps leading to failure, pre-initiation deformation, crack initiation and crack propagation, are affected. For still other cases only the crack initiation and early propagation processes are affected. This paper attempts to evaluate the mechanisms which have been proposed for environmental effects on the early stages of fatigue damage, including crack initiation and early propagation in gaseous and in aqueous environments. Evidence is presented which indicates that there is no unifying theory of environmental fatigue, but that each alloy/environment couple may exhibit significantly different behavior, depending on factors such as thermodynamics and kinetics as well as microstructure, slip character, etc.

Introduction

The imposition of cyclic stresses on metallic materials results in the well known phenomenon of fatigue, a degradation process which has been extensively studied by metallurgists, mechanical engineers and scientists interested in solid mechanics. However, it is also well known that environment can play a decidedly important role on fatigue crack initiation and crack propagation. Several recent reveiws have addressed the historical aspects of environmental fatigue. (1-7) both from a crack initiation and crack propagation point of view. Accordingly, in view of the relatively small number of investigations which are currently underway, it will not be the intent of this presentation to repeat those reviews in depth. Additionally, since the issues of macro-crack propagation are discussed by Wei and Speidel (this conference), and attempt will be made to concentrate on the relatively unknown aspects of environmental crack initiation and early growth. Also, while effects at elevated temperatures are very important, attention will primarily be addressed at effects which occur at or near room temperature.

Gaseous Environments

In general, gaseous environments at or near room temperature are not considered to be particularly important in affecting fatigue crack initiation processes. (2) Exceptions to this hypothesis, however, have been observed, particularly in aluminum alloys, although some of the reported results may be controversial. For example, some investigators have shown that, in air versus vacuum or inert atmosphere tests, S-N curves diverge with decreasing stress, showing a lower fatigue limit (8-10) while, for other metals and alloys, S-N curves converge with decreasing stress showing essentially the same fatigue limit. (11,12) Clearly for the first case, if the fatigue limit

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There have been a number of interpretations of how gaseous environments might affect crack initiation. For example, early investigators suggested that fatigue generated slip bands must produce a large vacancy concentration and, accordingly, must dissolve significant amounts of oxygen, on other gaseous species from the environment. This dissolved gas leads to dilatational strains, slip irreversibility and prevents rewelding of mascent cracks. (Fig. 1) It may be significant that most of the early work was performed on relatively high purity metals and alloys, which tend to exhibit wavy slip. Aluminum alloys, on the other hand, tend to exhibit planar slip, but present the complication that they are also highly reactive and tend to form thin solid films very quickly. The role of such films can be expected to be very significant in planar slip materials where significant numbers of dislocations egress the surface in each cycle. The dislocation egress forms large slip steps of virtually un-reacted material, and the reaction kinetics and nature of the reaction product film would conceivably have marked effects on surface deformation and subsequent crack nucleation depending on the mechanism of crack formation. For example, a comparison between the surface deformation behavior of aluminum under fatigue loading in laboratory air versus a vacuum on the order of 10^{-9} torr showed significant differences. In both cases the aluminum was filmed; however, relatively intense slip was observed in air, while more homogeneous, less intense slip was observed in vacuum. (Fig. 2) Measurements of the oxide film modulus indicated a fourfold increase in elastic modulus for a film tested in vacuum compared with a film tested in

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air, presumably due to water molecules which are included in the film in contact with laboratory air. Thus the higher stiffness of the film tested in vacuum presumably inhibits the formation of surface slip steps. How this procedure affects crack nucleation, however, is not necessarily obvious and should depend on the intrinsic properties of films which are formed. There are several possibilities, for example:

- (1) If the film is brittle, reoxidation rates are low and local strains are sufficiently intense, local rupture of the films may result in large slip offsets and enhanced crack nucleation. (Fig. 3).
- (2) If the film is ruptured by local plastic deformation and reoxidation rates are high, reverse slip may be inhibited leading to enhanced surface deformation. (Fig. 4)
- (3) The film may be sufficiently strong and/or ductile to restrain surface deformation under these circumstances secondary slip systems may be activated to accommodate strain, leading to more homogeneous surface deformation. Such a result has been observed for nickel base alloy single crystals at elevated temperatures. (Fig. 5) (13)
- (4) The presence of the oxide film may result in void formation in the metal or alloy below the film this resulting in premature nucleation under the film. (Fig. δ) (14)

Few of these hypotheses have been critially examined, but it is obvious that there is probably no single mechanism which governs crack nucleation for all classes of metals and alloys. Rather, the deformation character of the alloy the thermodynamics and/or kinetics of film formation the mechanical properties of surface films and the mode of fatigue crack nucleation all interact to determine the sensitivity of the fatigue crack nucleation phenomenom.

While little effort has been directed toward studying the effects of gaseous environment on high strain fatigue crack initiation, several investigations have shown that oxide produced at elevated temperatures can have significant effects. Intergranular crack nucleation in stainless steels at high temperatures has been attributed to the effect of an oxideinduced notch created during preheating of the alloy. (Fig. 7) (15) Oxide cracking in preferentially oxidized grain boundaries of nickel base superalloys has also been suggested to accelerate low cycle fatigue crack initiation in air at elevated temperatures. (16) Coffin has suggested that virtually all of the degradation in fatigue life at elevated temperatures of a number of materials can be attributed to environmental interactions. noting that frequency effects in the low cycle fatigue law could be eliminated for a large number of metals and alloys by testing in vacuum.(Fig. 8) (17) Additionally, it was noted that tests performed in vacuum showed transgranular crack nucleation and propagation versus intergranular nucleation and propagation in air at elevated temperatures. These results are not unambiguous since Koburger has shown a frequency effect in high cycle fatigue for directionally solidified eutectic alloys when tested in air and in vacuum, particularly at elevated temperatures. (18) The primary difference in these results may be related to the lack of intergranular cracking in the eutectic alloys.

Not all investigators agree that gaseous environments affect the crack nucleation process. For example, Wadsworth and Hutchings showed that the appearance of intrusions, extrusions and microcracks was similar in air and in vacuum for an equivalent number of cycles, although further development of these features was very much reduced. (8) Hordon, investigating the fatigue behavior of aluminum in vacuum, has expressed the opinion that not only initiation, but the entire Stage I propagation step

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is unaffected by environment, while adsorption of oxygen at the tip of a growing crack increases Stage II propagation and thus reduces fatigue life. (19) Laird and Smith, on the other hand, agree that crack initiation in pure metals is unaffected by environment, but observed that the early stages of crack growth are increased by air, the effect becoming less pronounced as the crack growth proceeds: (20) they attributed this increase to chemical attack of the crack tip. Achter (31), and Latanision and Westwood (22) have also related the environmental effect to the propagation stage rather than the initiation stage.

In view of the rapid contamination of metallic surfaces by gaseous environmental adsorbates, critical experiments remain to be performed to understand the effects of gaseous environments on fatigue crack nucleation. For example, monolayer oxygen coverage of newly generated surfaces in air occurs in microseconds and even if a relatively good vacuum is obtained (of the order 10⁻⁶ torr), surface coverage will occur in only a few seconds. Since the fatigue crack initiation process has been shown to be a relatively slow step involving thousands of cycles at moderate applied stresses, it is evident that crack initiation in practice rarely occurs without an oxidizing environment being present. While it may be possible to examine crack initiation as a function of environment if ultrasonic frequencies are combined with ultra high vacuum, the effects of gaseous atmospheres on nucleation remain to be resolved. It should be emphasized, however, that from available data, the effect of gaseous environments (if one exists) on crack nucleation is very small compared to the effect on crack propagation for most metals and alloys.

Once a crack has nucleated, * several possibilities can occur which may be regarded as environment sensitive. Many if not most metals and

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alloys exhibit stage I or crystallographic cracking in the early stages. A few highly planar slip materials show stage I cracking throughout the crack growth process. However, the majority of alloys which are studied generally show a shift to stage II cracking a few microns from the free surfaces. This transition is sometimes affected by environmental considerations. For example, experiments conducted on stage I crack propagation in single crystals of a precipitation hardened aluminum alloy (Al-Zn-Mg), in dry nitrogen and in laboratory air have shown a strong effect of frequency for the latter environment but not for the former. (Fig. 9) Since the environmental effect in this case is believed to be water vapor induced hydrogen embrittlement, the frequency effect may be explained by the time available for hydrogen to diffuse into the alloy to create local embrittlement. Other studies have shown that the plastic zone associated with the tips of short cracks are also affected by environment and accordingly effect early crack growth. (25) For some systems these effects are only observed for early crack growth (Fig. 9) and mild environments do not affect the growth of large fatigue cracks. (26) It may be speculated that these effects are observed only when the crack tip plastic zone size is small, and thus local crack tip plasticity is readily affected. When crack tip plastic zones are large, the environmentally affected characteristics of plastic deformation may be dominated

*The transition between nucleation and early crack propagation is, of course, rather ill defined. Whether or not the effects of the first vestiges of an intrusion on the stress intensity associated with persistent slip bands can be regarded as nucleation is a matter of opinion. It is also appropriate here to disgress briefly on the definitions of stage I and stage II fatigue cracking. Many investigators consider stage I cracking to be crack paths which are oriented at some finite angle with the free surface, and stage II cracking to be normal to the free surface. Others, this author included, consider stage I cracking to be crystallographic while stage II cracking occurs microscopically normal to the applied stress axis. Thus a crack which is macroscopically normal to the stress axis but can be identified with specific crystallographic facets on a microscopic level would be considered to be stage I cracking. This distinction is made since this author believes that the micro-mechanisms of fatigue crack propagation are different for the two types of cracking.

by gross plasticity effects.

Aqueous Environments

Theories of aqueous corrosion fatigue crack nucleation have generally relied on one or more of the following mechanisms: 1) stress concentrations at the bases of hemispherical pits created by the corrosive medium,

2) electrochemical attack at plastically deformed areas of metal, with nondeformed metal acting as a large area cathode, 3) electrochemical attack at ruptures in an otherwise protective surface flim, and 4) lowering of surface energy of the metal (particularly at growing crack tips), due to environmental adsorption leading increased propagation rates of microcracks.

Early investigators of corrosion fatigue (27,28) favored the stressconcentration pit theory, based on the physical examination of failed specimens which revealed a number of very large cracks originating at large hemispherical pits at the metal surface. Pit formation in metals and alloys in aggressive environments undoubtedly does lead to a reduction in fatigue life. However, it is important to note that the corrosion fatigue phenomenon also occurs in environments where pitting does not occur. For example, low carbon steels are highly susceptable to corrosion fatigue in acid solutions where pits are not observed. (29,30) Additionally. reduced fatigue lives can be induced in steel specimens by the application of small anodic currents in deaerated solutions where pits do not form. Fatigue tests performed in 3 percent NaCl+NaOH solution of pH 12, where a number of randomly distributed pits are observed, show fatigue limits identical with those observed in air. (31) Results of this kind are perhaps not unexpected since corrosion induced pits tend to be hemispherical in nature and the stress intensity factor associated with surface connected

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hemispherical defects is not large.

In order to examine the corrosion fatigue crack initiation process, low carbon steels fatigued in neutral 3 percent NaCl solutions for small percentages of total fatigue life were sectioned and examined metallographically. Although some hemispherical pits were observed in the specimen surface, no cracking could be attributed to their presence. Rather, accelerated corrosion of initiated stage I cracks was noted, with a deep "pit-like" configuration being oriented at approximately 45° to the specimen surface. No fatigue cracks were observed emanating from these pits, and an examination of specimens cycled for longer periods showed that the extent of growth of initiated fatigue cracks was always equivalent to "pit" depth, with no "normal" fatigue cracks associated with pits. It may be concluded then, that in many cases, the pits observed at failure by previous observers are not the cause of corrosion fatigue cracking but rather the result. (32)

On the basis of a series of corrosion fatigue experiments performed on cold worked and annealed steel wires, Whitwham and Evans suggested that failure is due to distorted metal acting as anode with undistorted metal acting as cathode; very fine cracks advancing by a combination of electro-chemical-mechanical action. (33)

Surface film rupture as the principal cause of the corrosion fatigue phenomenon of steels has been also proposed. Evans and Simnad (30,33), also suggested that film rupture might be important in neutral solutions but that structural changes in the metal predominate in acid solutions (distorted metal as anode). The electrode potential of a steel has been observed to become more active in fatigue tests with a higher rate of change being noted at higher stresses. This potential drop continues throughout a particular alternating stress experiment, but reaches a

steady-state in static tests. This observation has been attributed to the destruction of a protective film. (34)

Experiments conducted on low carbon steels in chloride have shown that there appears to be a critical corrosion rate associated with the onset of corrosion fatigue and that this corrosion rate is not a function of applied stress level. (31) (It has been shown that this "critical" rate has no fundamental meaning since general corrosion does not occur over the entire specimen surface. (35) Additionally it was shown that steels could effectively be cathodically protected from corrosion fatigue either above or below the fatigue limit at a potential which corresponds to that which is normally observed for cathodic protection independent of the applied stress level. This observation suggests that there is no fundamental thermodynamic shift in the equilbrium potential of the iron. Additionally corrosion fatigue was observed to occur in acid solutions where adherent films are unstable, thus suggesting that film rupture cannot be accepted as a general mechanism for corrosion fatigue.

Experiments performed on polycrystalline pure copper (which does not exhibit a reduction in fatigue resistance under free corrosion conditions) showed that increasing corrosion rates, by applying anodic currents, result in a reduction of fatigue resistance in a similar manner to that observed for steels. (36) A "critical" corrosion rate also was observed. (Fig. 10) (At very high corrosion rates, there is a reversal in fatigue resistance due to rapid blunting of nascent cracks.) Examination of the free surfaces showed that, while slip band crack initiation was observed in sir, free corrosion resulted in mixed transgranular-intergranular cracking and applied anodic currents resulted in totally intergranular failures. Slip bands were shown to be preferentially corroded and there appeared to be an increase in both the magnitude and density

of emerging slip bands. These data indicate that it is the local rather than the general corrosion rate which is critical. Figure 11 shows metallographic cross-sections of the copper and clearly shows the intergranular nature of the corrosion fatigue cracking and the increase in clip offset height under corrosion fatigue conditions. (37) Corrosion fatigue experiments conducted on single crystals of identical orientation showed an increase in corrosion fatigue resistance under conditions of applied current and an approximately twofold increase in the magnitude of slip step offsets. The character of the slip offsets is also affected, with clusters of persistent slip bands occurring in air and a more uniform distribution of active dissolution. (Fig. 12)

Analysis of the results obtained for steels and copper indicated that corrosion fatigue crack initiation occurs by two steps; (a) persistent slip bands are preferentially attached leading to stress intensification and subsequent early crack propagation and (b) corrosion results in a significant increase in the density of persistent bands which produce numerous crack initiation sites. The latter observation presumably occurs because metal atoms associated with mobile dislocations in the persistent slip bands are more active than surrounding metal atoms, leading to strain relief in the surface and significant increases in surface deformation.

A simple model of this process is schematically shown in Fig. 13. Rollins and Pyle have also observed active current spikes associated with slip band emergence in passive stainless steels, with subsequent repassivation occurring if strain is held constant. (36,37) Current spikes are observed in both tension and compression modes of deformation, although the effect is greater in the tensile half of the cycle.

The observation that polycrystalline copper fails in an intergranular manner under corrosion fatigue conditions suggests that the enhanced deformation

associated with grain boundaries causes enhanced preferential dissolution of the grain boundaries relative to emerging slip bands. Single crystals of copper show improved corrosion fatigue resistance due to crack blunting. In steels, on the other hand, preferential grain boundary attach is not observed and corrosion fatigue failures are accordingly transgranular.

The fatigue resistance of high strength aluminum alloys is also severely affected by corrosive solutions, particularly in chloride solutions, and this behavior has generally been attributed to either preferential dissolution at the tips of growing cracks or to preferential adsorption of a damaging ionic species. (38-40) Recent experiments on a 7075-T6 commercial alloy and on a high purity analog of the alloy (Al-5.0Zn-2.5Mg-1.5Cu) indicate that localized hydrogen embrittlement may be responsible for the poor corrosion fatigue resistance of these alloys. For example, Fig. 14 shows the results of fatigue tests performed on the 7075 alloy under simultaneous exposure to cyclic stresses and a corrosive environment (curve B) compared to tests performed in laboratory air (curve A). If specimens are pre-corroded and tested in laboratory air, there is also a significant reduction in fatigue resistance (curve C). $^{(41)}$ The reduction in life at low N_f is associated with pits which form at non-metallic inclusions. If the alloy is resolutionized and aged, equivalent to a low temperature bake, a significant amount of fatigue resistance is regained, indicating at least partial reversibility of the damaging phenomenon and strongly suggesting a solid solution effect arising from environmental interaction. Additionally, the reversibility in fatigue resistance is a function of baking time. (41) Hydrogen is the only stable gaseous species at the corrosion potential of the alloy and gas bubbles were observed to emanate from growing cracks.

It had been previously observed that halide ions are particularly damaging to the fatigue behavior of Al alloys, however, if the alloy is cathodically charged during stressing, sulfate ion proves to be equally damaging, particularly at long N_f. At lower N_f the slight decrease observed in Cl solutions appears to be associated with damage to the passive film. (Fig. 15) In SO 4 solutions, a crack must initiate to break the protective film to allow access to the bulk alloy. (42,43) Cathodic charging of the high purity analogue of the 7075 alloy also shows a reduction in fatigue resistance. In many cases, fatigue crack initiation in the equi-axes grain high purity alloy is intergranular, and at more active cathodic potentials there is a tendency toward a higher percentage of transgranular cracking.

The relative amount of intergranular cracking is also a function of applied stress levels and, for the most active condition, lower stresses lead to an increased amount of intergranular cracking. This data indicates that there is a relationship between stress corrosion cracking of the alloy and corrosion fatigue, and that there is a competition between transport of hydrogen to grain boundaries and hydrogen interacting with growing transgranular cracks. At long lives or for rapidly propagating cracks hydrogen cannot diffuse to grain boundaries and thus interacts with the tips of growing transgranular cracks. Stress corrosion cracking of a similar alloy has been associated with hydrogen cracking by Swann and co-workers. (44)

It has been argued that bulk aluminum alloys should not be hydrogen embrittled since the solubility and diffusion rates of hydrogen in aluminum are relatively low, however, the sub-critical crack growth in aluminum alloys need only propagate into the region immediately ahead of a growing crack to affect propagation rates. It has also been suggested that

accelerated transport of hydrogen might occur by dislocation motion $^{(45,46)}$, and tensile tests of the high purity alloy under cathodic charging conditions in $1N\ H_2^{SO}_4$ + As show serrated yielding in contrast to tests performed in air.

Finally, experiments performed on a commercial 7075 alloy in a mode III loading condition (torsion), indicated that the reduction in fatigue resistance associated with cathodic charging was considerably less than under mode I loading. (Fig. 16) Although total immunity to corrosion fatigue was not observed, the slight reduction in fatigue resistance can be associated with conditions which did produce a true mode III loading condition both on a micro-scale and on a macro-scale. (47)

To summarize the Al alloy results, it appears that corrosion reactions liberate hydrogen, which effectively embrittles the region in the vicinity of a crack tip. The specific details of the embrittlement are not known, but it appears that dislocation transport of the hydrogen is involved. It has been speculated that hydrogen may collect at the semicoherent precipitate-matrix interface, thus explaining the reported (100) fracture plane, however, a great deal more research will have to be performed before a more definitive answer will be available.

Conclusions

In conclusion, it is obvious that many factors interact to affect crack nucleation and early growth either in gaseous or in aqueous environments. The exact role of most of these parameters is relatively unknown. However, recent data shows that basic deformation modes can be altered by environment and for many systems these fundamental effects are most important in the crack nucleation/early growth steps. It is this area of the environmentally affect deformation process which appears to be the most fruitful for future investigation.

ACKNOWLEDGEMENTS

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- D. J. Duquette in "Corrosion Fatigue, Chemistry, Mechanics and Microstructure", ed. O. Deverent, A. McEvily and R. Stachle, NACE, Houston 1972, p. 12.
- 2. C. Laird and D. J. Duquette ibid p. 88.
- 3. R. P. Wei in "Fatigue Mechanisms" STP 675 ed. J. Fong ASTM, Philadelphia, 1979, p. 816.
- D. J. Duquette in "Mechanisms of Environment Sensitive Cracking Of Materials" Ed. P. Swann, F. P. Ford and A. R. C. Westwood, The Metals Society, London, 1977, p. 305.
- 5. D. J. Duquette in "Environment Sensitive Fracture of Engineering Materials" ed. Z. A. Foroulis, AIME, New York, 1979, p. 521.
- 6. D. J. Duquette in "Fatigue and Microstructures" Am. Soc. for Metals, Metals Park, 1979, p. 335.
- 7. H. A. Marcus in "Fatigue and Microstructure" Am. Soc. for Metals, Metals Park, 1979, p. 365.
- 8. N. J. Wadsworth and J. Hutchings, Phil. Mag., 3, 1154, (1958).
- 9. N. J. Wadsworth, Phil. Mag. 6, 387, (1961).
- 10. N. Thompson, N. J. Wadsworth and N. Louat, Phil. Mag. $\underline{1}$, 113, (1956).
- 11. J. M. Jacisin, Trans. TMS-AIME 239, 1967, p. 821.
- 12. W. Engelmaier, Trans. TMS-AIME 242, (1968), p. 1713.
- 13. D. J. Duquette and M. Gell, Met. Trans. 2, (1971), p. 1325.
- 14. H. Shen, S. E. Podlaseck and I. R. Kramer, Acta Met., 14, p. 341, (1966).

- 15. B. Hodgson, Met. Sci. J., 2, p. 235, (1968).
- 16. C. J. McMahon and L. F. Coffin, Jr., Met. Trans, 1, p. 3443, (1960).
- 17. L. F. Coffin, Jr., Met. Trans. 3, p. 1777, (1972).
- C. Koburger, Ph.D. Dissertation, Rensselaer Polytechnic Institute,
 September 1978.
- 19. M. J. Hordon, Acta. Met. 14, p. 1173, (1966).
- 20. C. Laird and G. C. Smith, Phil. Mag. 8, p. 1945, (1963).
- 21. M. Achter, in 415, ASTM, Philadelphia, 1967, p. 181.
- R. M. Latanision and A. R. C. Westwood, Advances in Corrosion Science and Technology, Plenum Press 1967, p. 80.
- 23. M. Nageswararao, R. Meyer, M. Wilhelm and V. Gerold in "Mechanisms of Environment Sensitive Cracking of Materials", Ed. P. R. Swann, F. P. Ford and A. R. C. Westwood, The Metals Society, London, 1977, p. 383.
- 24. M. Wilhelm, M. Nageswararao and R. Meyer in "Fatigue Mechanisms"

 STP 675, Am. Soc. for Testing and Materials, Philadelphia, 1979, p. 214.
- 25. S. P. Lynch in "Fatigue Mechanisms" STP 675, ASTM, Philadelphia, 1979, p. 174.
- 26. D. L. Davidson and J. Lankford in "Environment Sensitive Fracture of Engineering Materials Ed. Z. A. Froulis AIME, New York, 1979, p. 581.
- 27. D. J. McAdam, Jr. and G. W. Geil, Proc. Am. Soc. Test. Mat., 41, p. 696 (1941).
- 28. B. B. Westcott, Mech. Eng. 60, p. 813, (1938).
- 29. H. Spahn, Metalloberflache, 16, p. 299, (1962).
- 30. M. T. Simnad and U. R. Evans, Proc. Roy Soc. A188, p. 372, (1947).
- 31. D. J. Duquette and H. H. Uhlig, Trans. ASM, <u>62</u>, p. 839, (1969).
- 32. D. J. Duquette and H. H. Uhlig, Trans. ASM, <u>61</u>, p. 449, (1968).
- 33. D. Whitwham and U. R. Evans, J. Iron and Steel Inst., 165, p. 72, (1950).
- 34. A. V. Ryabchenkov. Zhur. Fiz. Khim, 26, p. 542, (1952).
- 35. N. H. Hahn and D. J. Duquette, Acta Met., 26, p. 279, (1978).
- 36. V. Rollins and T. Pyle, Nature, <u>254</u>, p. 322, (1975).

- 37. T. Pyle, V. Rollins and D. Howard, J. Electrochem. Soc., <u>122</u>, p. 1445, (1975).
- 38. R. E. Stoltz and R. M. Pelloux, Met. Trans., 3, p. 2433, (1972).
- 39. R. M. Pelloux, "Fracture 1969", Proc. Int. Conf. on Fracture, Brighton, Chapman and Hall, 1969.
- 40. R. J. Selines and R. M. Pelloux, Met. Trans. 3, p. 2525, (1972).
- 41. E. F. Smith, III, R. Jacko and D. J. Duquette, in "Effect of Hydrogen on Behavior of Materials", Ed. A. W. Thompson and I. M. Bernstein, AIME, 1976, p. 218.
- 42. R. J. Jacko and D. J. Duquette, Met. Trans. 8A, p. 1821. (1977).
- 43. E. F. Smith, III, R. J. Jacko and D. J. Duquette, "Proc. 2nd. Int. Congress on Hydrogen in Metals", Paris, 1977, paper 3Cl.
- 44. L. Montgrain and P. R. Swann, in "Hydrogen in Metals", Ed. I. M. Bernstein and A. W. Thompson, ASM, Metlas Park, 1974, p. 575.
- 45. J. K. Tien, in "Effects of Hydrogen on Behavior of Material", Ed.

 A. W. Thompson and I. M. Bernstein, ASM, Metals Park, 1974, p. 207.
- 46. H. H. Johnson and J. P. Hirth, "Met. Trans.", 7A, p. 1543, (1976).
- 47. R. J. Jacko, Ph.D. Dissertation, Rennselaer Polytechnic Institute, Troy, N.Y., August 1978.

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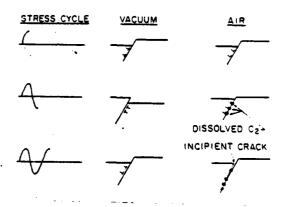


Figure 1. Model of oxygen/slip band interaction to explain environment sensitive fatigue crack nucleation.

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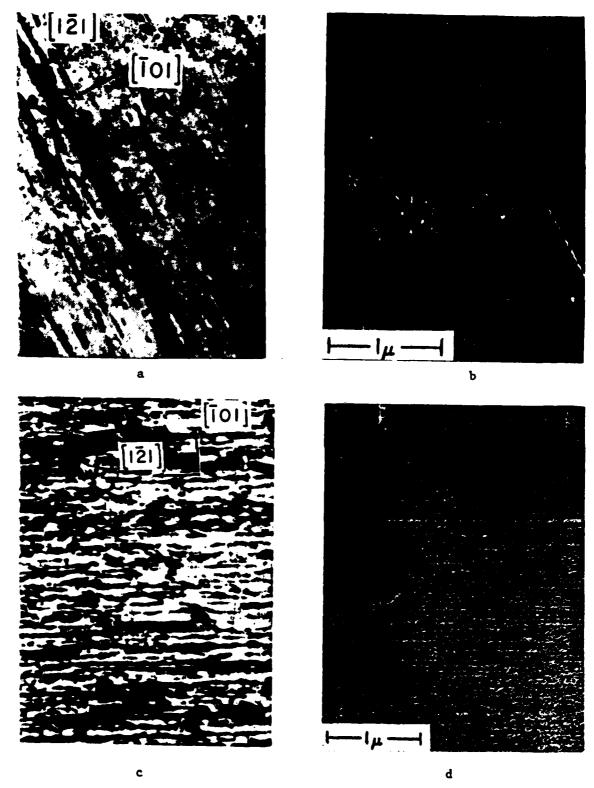


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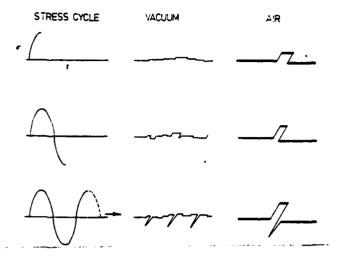


Figure 3. Schematic diagram of surface film interaction with crack nucleation. Once the film has ruptured, the energent slip band is "soft" and deformation will preferentially occur in this region.

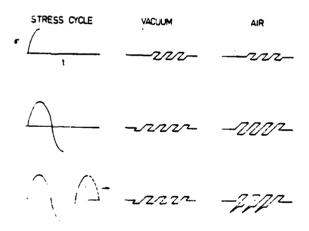
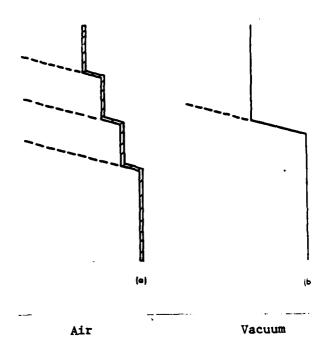
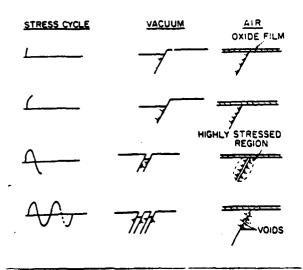


Figure 4. Schematic diagram of oxidation interaction with surface deformation. This process would lead to a "racheting" effect inhibiting reverse slip.

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Schematic diagram of surface film inhibiting Figure 5. slip and crack nucleation.



Model of void nucleation under oxide films to Figure 6. accelerate crack initiation in gaseous environments.

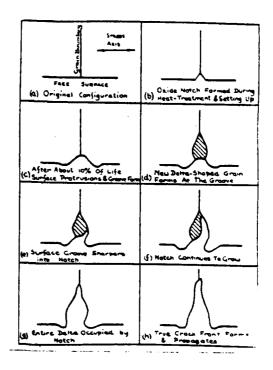


Figure 7. Model for fatigue crack nucleation in stainless steel at elevated temperature suggesting that an oxide created notch nucleates a new grain and subsequent crack nucleus.

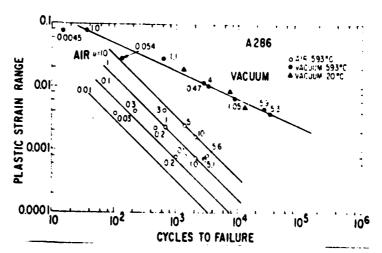


Figure 8. Plastic strain range vs. fatigue life for A286 ferrous alloy in air and in vacuum at 593°C. Numbers adjacent to test points indicate frequency in cpm. Note absence of frequency effects in vacuum.

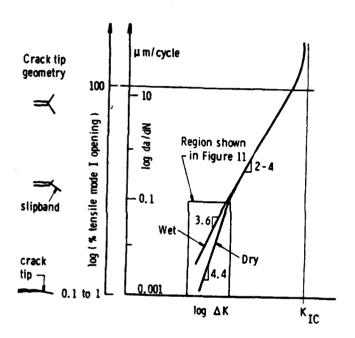


Figure 9. Schematic relationship between crack opening mode, extent of plastic zone and environmental effects in crack growth in mild steel exposed to wet air and dry nitrogen. Note that the increase in crack propagation rate is only observed at short crack lengths (small plastic zone size and planar slip).

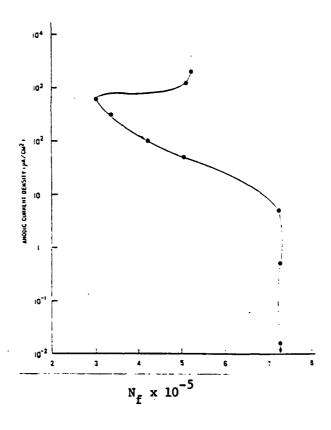
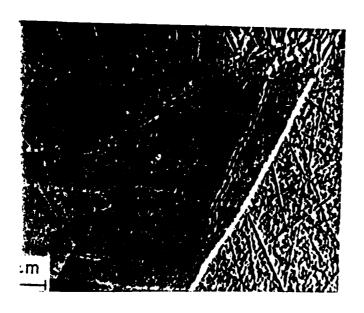


Figure 10. The effect of applied anodic current on fatigue behavior of OFHC copper. Note the fatigue life independent region up to \sim 10 $\mu\text{A/cm}^2$ and also the increase in fatigue life at currents greater than \sim 10 3 $\mu\text{A/cm}^2$.



(a) air showing transgranular cracking



(b) in 0.5N NaCl showing mixed, but predominantly intergranular cracking

Figure 11. Longitudinal metallographic cross sections of fatigued Cu

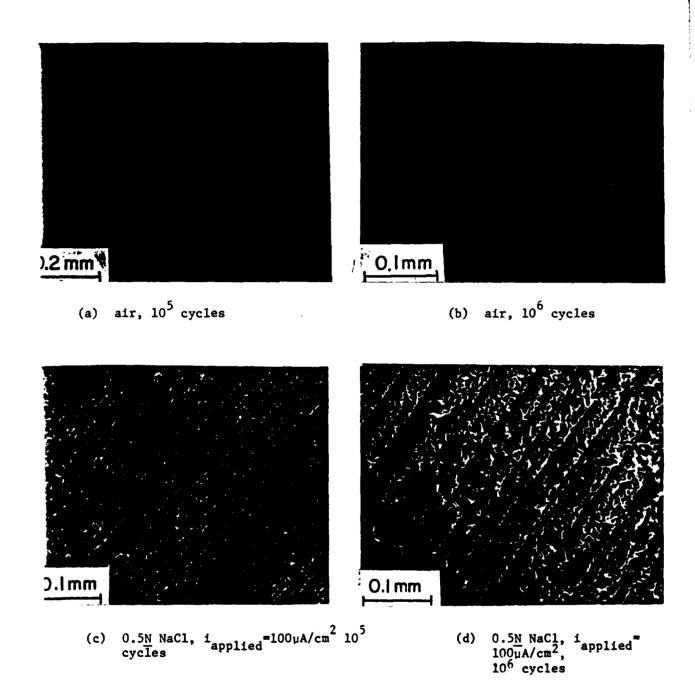
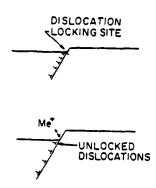
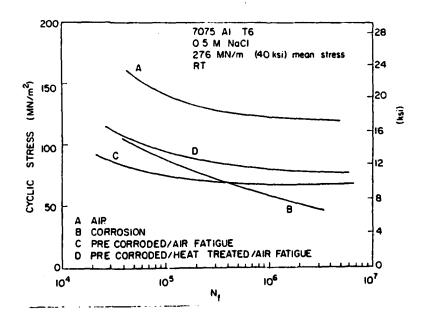


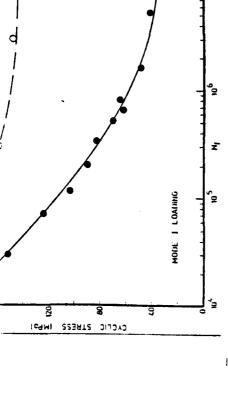
Figure 12. Copper single crystal surface slip offset appearance

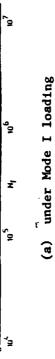


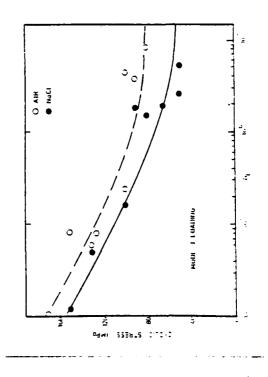
Schematic illustration of corrosion Figure 13. affected fatigue crack nucleation.



The effects of corrosion and pre-corrosion Figure 14. on the fatigue lives of a 7075-T6 alloy. Note that re-solutionizing and re-aging the alloy after precorrosion results in a significant increase in fatigue resistance.







Effect of cathodic polarization on the fatigue behavior of 7075 Al alloy in NaCl and ${\rm Na_2^{SO}}_4$.

Figure 15.

(b) under Mode 3 loading

Figure 16. Fatigue behavior of 7075 Al alloy in air and in aerated NaCl solution,

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3. ABSTRACT

It is well known that environment plays a very important role in fatigue failures. In some cases only crack propagation rates are affected; however, for many others all of the steps leading to failure, pre-initiation deformation, crack initiation and crack propagation, are affected. For still other cases only the crack initiation and early propagation processes are affected. This paper attempts to evaluate the mechanisms which have been proposed for environmental effects on the early stages of fatigue damage, including crack initiation and early propagation in gaseous and in aqueous environments. Evidence is presented which indicates that there is no unifying theory of environmental fatigue, but that each alloy/environment couple may exhibit significantly different behavior, depending on factors such as thermodynamics and kinetics as well as microstructure, slip character, etc.

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